A PRIORI SIMULATION OF COAL PYROLYSIS EXPERIMENTS BASED ON COAL ELEMENTAL COMPOSITIONS

Yuxin Zhao, Michael A. Serio, and Peter R. Solomon
Advanced Fuel Research, Inc.
87 Church Street, East Hartford, CT 06108, U. S. A.

Keywords: Coal Pyrolysis, Modeling, Tar Yields.

INTRODUCTION

Coals come in various ranks and from different geological origins. Substantially different characteristics are commonly observed for coals of different ranks. Coal samples from the same seam can exhibit large variations in their devolatilization and related thermal and combustion behavior. Such variations have large impacts to the design and operating conditions of coal combustion systems. It is imperative that coals are well characterized before their utilization. This normally requires sophisticated instrumentation and special expertise, which are not likely available in a single laboratory. Robust methods of predicting coal devolatilization behavior before invoking expensive experiments can be of practical importance.

Recently, there have been developments of several coal devolatilization models [1-6], which have various capabilities of predicting coal thermal decomposition under practical conditions. A common shortcoming of these models is that they require a large set of data input, including kinetic parameters, gas precursor compositions and additional parameters describing the coal polymeric structure. These input data must be generated based on a series of experimental measurements for each coal of interest. Predictions are limited to coals that have been studied. This limitation has long been criticized although it originates from the complicated nature of the coal structure. On the other hand, some investigators have tried to correlate the devolatilization properties to the coal types. For instance, Ko et al. [7] and Neavel et al. [8] have developed methods of predicting the upper bound of tar yields, X_{tar}, from coal elemental compositions. The predicted X_{tar} can be used as an input parameter of general tar kinetic models such as those developed by Serio et al. [9] and Suuberg et al. [10]. Niksa and Kerstein [11,12] have also proposed a correlation method for the FLASHCHAIN coal devolatilization model which predicts tar and the total volatile yields in pyrolysis based on ultimate analysis.

This paper presents a general method that provides a direct correlation between coal elemental compositions and the input parameters of a general coal devolatilization model, FG-DVC [1-3], which can predict, in addition to the tar and total volatile yields, the yields of individual gas species, the tar molecular weight distribution, and the char fluidity. This model was validated for the eight Argonne Premium coals based on measurements of pyrolysis kinetics from TG-FTIR analysis, solvent extraction and solvent swelling to measure extractables and initial crosslink density, respectively, Gieselar plastometer experiments to measure fluidity, pyrolysis-FIMS to measure the tar molecular weight distribution and ultimate analysis to determine the elemental compositions (C, H, N, S, O) [3]. The large number of experimental inputs allowed the development of a model which can make detailed predictions of coal devolatilization, as indicated above. However, this feature presented a difficulty when applying the model to unknown coals. The correlation method presented in this paper enables us to apply the FG-DVC model to coals of a wide range of types without prior knowledge of them except the elemental analysis, and supports our contention that the FG-DVC model is a general model that can perform expeditious evaluations of coal thermal decomposition under many heating and pressure conditions. This correlation approach in its preliminary form has been implemented into a 2-dimensional coal combustion model, PCGC-2 [13]. After a description of the method, the model predictions are compared with tar yield data collected at fast heating rates and various pressures from the literature [7, 14-21], and with tar yields at slow heating rates measured with TG-FTIR analysis in our laboratory.

BACKGROUND

FG-DVC [1-3] is a general coal devolatilization model that predicts coal thermal decomposition into light gases, tar and char. It also predicts other related property changes, i.e., coal viscosity and swelling, during pyrolysis. Recent improvements of this model have given it the ability to predict gaseous sulfur and nitrogen species evolved during pyrolysis [22]. The following is just brief description of this model, as the details have been published elsewhere [1-3, 22,23].

Coal has a very complicated structure, which is essentially a mixture of an aromatic matrix, side chain components and some loose fragments. The thermal decomposition of the coal structure involves many parallel and competitive processes. In modeling these

processes, FG-DVC uses two submodels. The FG model simulates the thermal evolution of various functional groups and the DVC model predicts the depolymerization, vaporization and crosslinking processes occurring in the coal polymer network. In the FG submodel, the gas evolution from functional group precursors is modeled with parallel first order differential equations and a distributed activation energy formulation is used to reflect the diversity of coal structures. The thermal evolution of the coal polymer matrix is modeled with a network model [2], which consists of nodes and the connections between them. The nodes represent the polymer clusters and there are two types of connections between them, i.e., bonds and crosslinks. At elevated temperatures, there is a competition between bond breaking and crosslinking. The properties of the network are fully determined by these two competing processes through percolation theory [24]. The most important property of the network is the molecular weight distribution of the clusters. The heavy molecules remain in the condensed phase to become char, while the light ones evaporate to become tar. The vaporization is calculated based on a mechanism given by Fletcher [25]. The tar rate is further limited by internal transport, which is assumed to be controlled by the total rate of gas species evolution plus the light tar [1]. This mechanism enables the model to predict the pressure variation of tar yields.

Input parameters are required to describe the coal structure and its evolution kinetics. Sets of parameters have been developed for the eight coals provided by the Argonne Premium Coal Sample Program [26], employing various analytical methods, including TG-FTIR, solvent swelling and extraction, fluidity, NMR, and FIMS.

CORRELATION APPROACH

The behavior of coal when subjected to a physical and chemical analysis or treatment exhibits rank dependence in most instances. For example, Solomon et al. [3] have shown a consistent variation of coal functional group compositions with rank. The basis of the correlation formulation presented here relies on the well-known van Krevelen diagram [27], which indicates that the progress of coalification in terms of the coal's atomic hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios forms a distinctive band in the H/C and O/C two dimensional plane. Each coal has a coordinate (O/C, H/C) in the van Krevelen diagram. Fig. 1 illustrates the variation of the vitrinite reflectance index (v.r.i.) as a function of H/C and O/C, for 45 PSOC coals sponsored by the U. S. Department of Energy. As v.r.i. is commonly accepted as a rank indicator, it is reasonable to assume that there exists a correlation between rank and elemental composition. Therefore, a parameter for an unknown coal can be interpolated from those for a set of coals that are well-studied. These well-defined coals are called library coals, a term used by Williams [28].

We propose to use a two dimensional linear interpolation method commonly used in finite element analyses, with O/C and H/C as two rank indicators. Let x be a parameter of an unknown coal and $x0(i)$ (i=1,N) are the corresponding parameters of the N library coals. The N library coals form a 2 dimensional triangular element mesh in the van Krevelen diagram as displayed in Fig. 2, where N is 9 with each node representing a coal. The mesh nodes are plotted as filled circles and other symbols in the plot are the coals to be interpolated. Each triangle element contains three nodes (coals). If an unknown coal is inside the element J, whose three nodal numbers are $i^{(1)}_J$, $i^{(2)}_J$, and $i^{(3)}_J$, the unknown parameter, x, is interpolated as

$$x=(1-r-s)\cdot x0(i_J^{(1)})+r\cdot x0(i_J^{(2)})+s\cdot x0(i_J^{(3)}) \qquad (1)$$

where r and s ($0\le r,\ s\le 1$) are the local coordinates of the unknown coal in element J and are determined from the positions of the unknown coal and the three interpolating coals in the van Krevelen diagram. Let U denote the point of the unknown coal in the van Krevelen diagram. $\Delta(i^{(1)}_J, i^{(2)}_J, i^{(3)}_J)$, $\Delta(i^{(1)}_J, U, i^{(3)}_J)$, and $\Delta(i^{(1)}_J, i^{(2)}_J, U)$ are the areas of the triangles formed by nodes $(i^{(1)}_J, i^{(2)}_J, i^{(3)}_J)$, $(i^{(1)}_J, U, i^{(3)}_J)$, and $(i^{(1)}_J, i^{(2)}_J, U)$, respectively. r and s are calculated as follows

$$r = \frac{\Delta(i_J^{(1)},U,i_J^{(3)})}{\Delta(i_J^{(1)},i_J(2),i_J^{(3)})}$$
$$s = \frac{\Delta(i_J^{(1)},i_J^{(2)},U)}{\Delta(i_J^{(1)},i_J(2),i_J^{(3)})} \qquad (2)$$

The interpolation mesh is composed of nine coals, six of which come from the Argonne Premium Coal Sample Program and three of which are PSOC coals (PSOC 1474, PSOC 1448, and PSOC 1521). Extensive experimental studies have been carried out on the Argonne Premium Coals and the model input parameters are well established [3].

Predictions of the pyrolysis yields of these coals under various conditions are in very good agreement with the data collected in many types of reactors [29]. The Lewston-Stockton coal was not used because it has a very similar elemental composition to the Pittsburgh Seam Coal. The Pocahontas #3 coal was not selected since it is of substantially high rank and is far away from the rest of the coals. Three PSOC coals were added to this mesh recently, so that a larger area is covered. The functional group compositions and the pyrolysis evolution kinetic parameters of these three coals were obtained based on data from TG-FTIR analysis and solvent extraction experiments performed recently in our laboratory and fluidity data from the PSOC coal data base.

With this scheme, any of the model parameters for the FG-DVC model can be interpolated for an unknown coal when its elemental composition is identified. Special caution must be used in interpolating the functional group compositions of the oxygen, sulfur and nitrogen gases in order to maintain a proper mass closure. For example, the total amount of the oxygen containing functional groups is limited by the oxygen content. Therefore, instead of interpolating the amounts of oxygen gas precursors directly, only the fraction of oxygen in a functional group is calculated and is used to compute the amount of this functional group from the oxygen content. The same procedure is followed for the sulfur and nitrogen gases.

TAR YIELD PREDICTIONS

Tar composes up to about 50% of the total volatiles during coal combustion for most coals. The secondary reaction of tar in the system produces soot, PAH, and light gases that affect ignition, flame stability and the radiative property of the flame. Tar yields vary with coal type and are affected by reactor conditions such as pressure and heating rate. The interpolation scheme presented above enables the FG-DVC model to predict the tar yield of a coal from its elemental analysis under various pressure and heating rate conditions. To verify this capability, tar yield data were assembled from literature and were compared with the model predictions. These data were measured with heated grid systems under fast devolatilization (heating rates from 100 °C/s to 1000 °C/s) for various coals and pressures (10^{-4} to 7 MPa). In addition to these data, tar yields from eight PSOC coals were measured with a TG-FTIR system at heating rate of 30 °C/min and atmospheric pressure. The details of the TG-FTIR system have been presented elsewhere [30]. The data used for model verification were selected to span a wide range of coal types, from lignite to low volatile bituminous, and pyrolysis conditions. Part of the data set was taken from the tabulation given by Ko et al [7].

For each of these coals, the FG-DVC input parameters were interpolated with the scheme proposed above and the tar yields from these coals were predicted with the pressures and the heating rates specified in these references. Eleven coals from the references and the eight PSOC coals are inside the mesh and the standard interpolations were performed. The Pocahontas, Illinois #6 and North Dakota lignite studied by Suuberg et al. [17] are outside the mesh and were predicted with the input parameters of the corresponding Argonne coals. The Alabama bituminous coal studied by Freihaut and Seery [15] and the Beulah Zap coal studied by Ko et al. [7] were predicted based on input files used for the Argonne Upper Freeport coal and Zap lignite, respectively. The Colstrip lignite by Reitzen [21] is close to the edge of the triangle formed by Zap lignite, Wyodak, and Illinois #6 coals, and was modeled with an elemental composition inside this triangle and closest to Colstrip.

The predictions and the data are compared in Fig 3. The standard errors of the estimates are 3.84%, 3.12%, and 3.38% for data collected at vacuum, atmospheric and high pressures, respectively. The total standard error of the estimate is 3.35%. This is in the same range of experimental scatter commonly encountered in tar measurements. The standard error the of estimate, σ, is calculated as follows:

$$\sigma = \sum_{1}^{N} \frac{(Y_i^m - Y_i^p)^2}{N}^{1/2} \qquad (3)$$

where Y_i^m and Y_i^p are the measured and predicted tar yields, and N is the number of data points compared.

Fig. 4 compares the predicted and the measured variations of tar and total volatile yields as a function of heating rate for a Linby coal studied by Gibbins and Kandiyoti [20]. For a Illinois #6 coal studied by Cai et al. [19], the variations of tar and total volatile yields as a function of heating rate and pressure were predicted and are compared with the data [19] in Fig. 5. These plots show that the predictions are in a reasonably good agreement with the data. It should be noticed that this is achieved based only on the elemental compositions

without further prior knowledge of these coals.

DISCUSSION

The success of this interpolation scheme depends on a thorough understanding of the library coals. Selection of these library coals must be performed with care so that none of these coals has peculiar behavior and deviates from coals in its rank. Although the current mesh contains only nine coals, it is one advantage of this method that it can be easily extended to include more coals. Adding more coals in the interpolation mesh will certainly increase the reliability of the predictions and will allow coverage of a wider range of coal types.

A few large discrepancies were observed for some coals, indicating needs for further improvements. Under-predictions of tar yields in vacuum were seen for a group of Pittsburgh seam coals, for which the measured tar yields are 39.0% [15], 37.0% [10] and 37.7% [18] and the predicted vacuum tar yields are 33.0%, 29.2% and 32.6%, respectively. However, good agreement was obtained at atmospheric pressure for these coals (26.5% [10] vs. 24.5% and 26.5% [17] vs. 26.9). Since the pressure variations are correctly predicted for other coals, the high vacuum tar yields for the Pittsburgh seam coals appear to be caused by a mechanism particular to these coals. The model also under-predicts tar yields for PSOC 1519 and 1492 coals. The Sesser sub-bituminous coal studied by Ko et al. [14] is the only coal that has a large over-predicted atmospheric tar yields (21.5% [14] vs. 27.0%). This coal seems to be an unusual coal as a relatively low tar yield was also reported by Reitzen [21] (11%). For most of the coals the predictions are within 3% of the data and the standard error of estimation calculated without the above large discrepancies is 2.54 wt%.

The basis of this interpolation method is the assumption that coals within the same rank behave similarly. Predictions based on this method are targeted at the normal or mean behavior of coals within the same rank. Deviations from normal, however, should be expected. If the deviation is large and can not be identified with an existing mechanism, the behavior of coals becomes unpredictable with the current method. The comparisons presented in Figs. 3 to 5 indicate that, for most coals, the deviations are small enough that the tar yields are well predicted. Some improvement may be achieved by including one additional parameter, such as the volatile matter content, in the correlation.

The yields and the compositions of the volatile gases are also important. The capability of FG-DVC in predicting the total volatile yields has been demonstrated in Figs. 4 and 5. The amounts of individual gas species are also predicted by FG-DVC along with the tar yields and this is one of the chief advantages of this model. However, comparisons are more difficult because of the relatively small amount of available data. This will be the subject of further studies.

CONCLUSIONS

An interpolation method was proposed to correlate the input parameters of a coal devolatilization model, FG-DVC, for untested coals, and is conceptually applicable to other devolatilization models. This method uses a set of well defined coals (library coals) to form a triangular mesh in the van Krevelen diagram. If an unknown coal is within a triangle formed by three library coals, the model input parameters for this unknown coal can be interpolated from those of the three library coals based solely on a knowledge of the elemental composition. This method allows the FG-DVC model to be used for any coal that can be interpolated. It is also easy to accommodate more library coals, so that a wider range of coal types can be covered.

The validity of this method was demonstrated by comparing the tar yields measurements and predictions for 27 coals under a wide range of pressures and heating rates. For most of the coals, the predictions compare very well with the data.

ACKNOWLEDGMENTS

This work was supported by the Morgantown Energy Technology Center of the US Department of Energy, through contract DE-AC21-86MC23075. The authors also wish to acknowledge helpful comments from Professor Eric M. Suuberg of Brown University.

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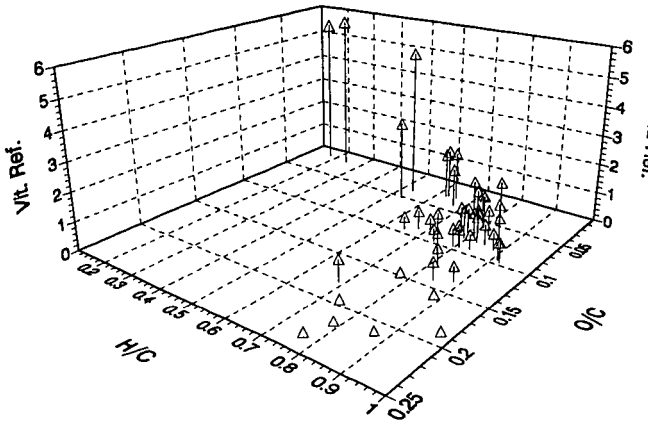

Figure 1. Variation of Vitrinite Reflectance of Coals from the PSOC DOE Sample Bank as a Function of H/C and O/C Ratios in the van Krevelen Diagram.

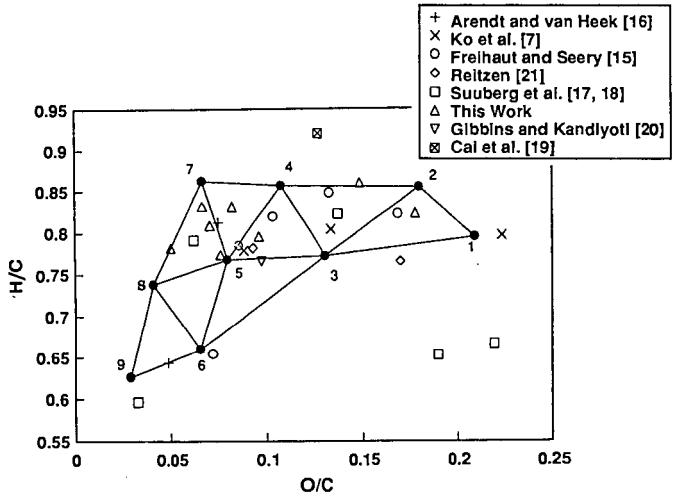

Figure 2. The Interpolation Mesh in the van Krevelen Diagram and Coals Used for Tar Yield Comparison. Argonne Coals: (1) Beulah Zap; (2) Wyodak; (3) Illinois #6; (4) Blind Canyon; (5) Pittsburgh #8; (6) Upper Freeport. PSOC Coals: (7) PSOC 1448; (8) PSOC 1474; (9) PSOC 1521.

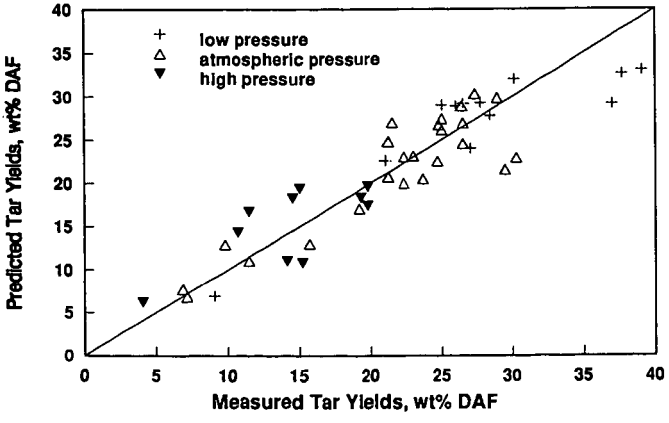

Figure 3. Comparison of the Measured and the Predicted Tar Yields for Coals Given in Fig. 2.

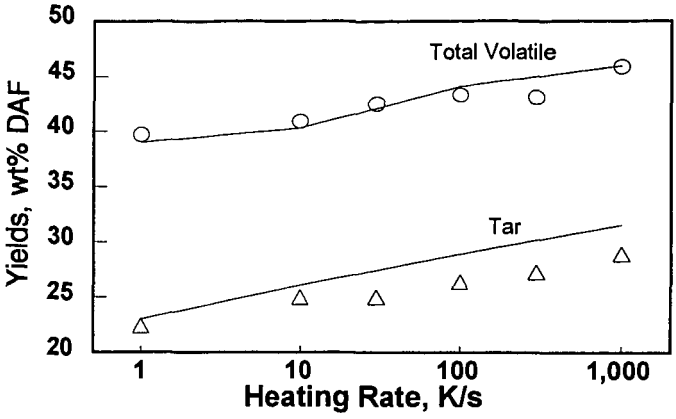

Figure 4. Variations of Tar and Total Volatile Yields as a Function of Heating Rate for a Linby Coal Studied by Cai et al. [19]. The Lines are Predictions and the Symbols are the Data.

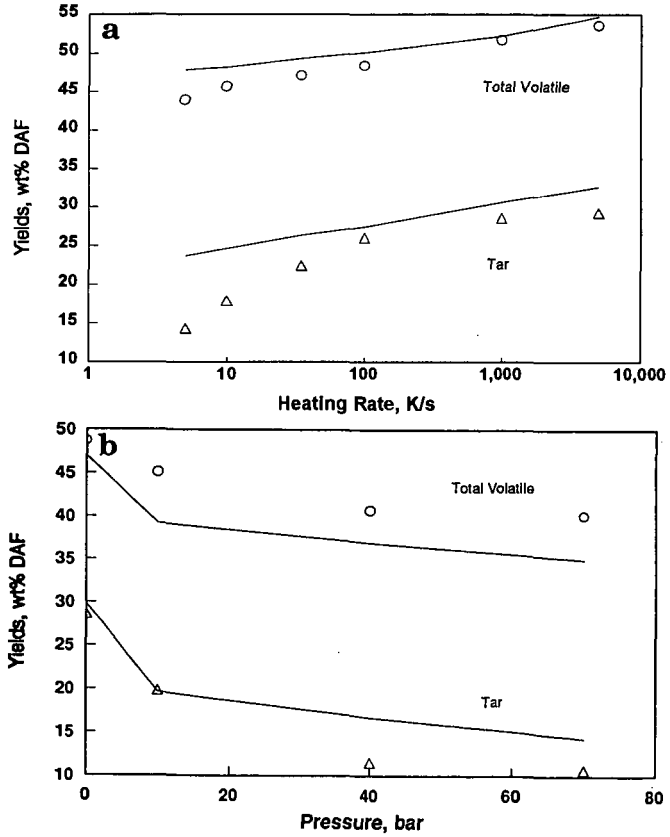

Figure 5. Variations of Tar and Total Volatile Yields as a Function of a) Heating Rate and b) Pressure for a Linby Coal Studied by Cai et al. [19]. The Lines are the Predictions and the Symbols are the Data.